Changes of the near-surface chemical composition of the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide room temperature ionic liquid under the influence of irradiation

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Radiation induced degradation effects are studied for a model ionic liquid (IL) – [EMIm]Tf_2N – in order to distinguish in which way the results of X-ray based material analysis methods can be falsified by the radiation supplied by typical X-ray sources itself. Photoelectron spectroscopy is commonly used for determining the electronic structure of ionic liquids. Degradation effects, which often occur *e.g.* in organic materials during X-ray or electron irradiation, are potentially critical for the interpretation of data obtained from ionic liquids. The changes of the chemical composition as well as the radiation-induced desorption of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]Tf_2N) fragments are analysed by X-ray photoelectron spectroscopy (XPS) as well as quadrupole mass spectroscopy (QMS) upon exposure to monochromated or non-monochromated AlKα X-rays from typical laboratory sources. During the irradiation of [EMIm]Tf_2N, an increasing carbon concentration is observed in both cases and especially the $[Tf_2N]^-$ ion is strongly altered. This observation is supported by the results from the QMS analysis which revealed a variety of different IL fragments that are desorbed during X-ray irradiation. It is shown that the decomposition rate is directly linked to the photon flux on the sample and hence has to be considered when planning an XPS experiment. However, for typical experiments on this particular IL the measurements suggest that the changes are on a larger time scale as typically required for spectra acquisition, in particular if monochromated X-ray sources are used.

Introduction

In recent years room temperature ionic liquids (RT-ILs) have attracted enormous interest since their special physical and chemical properties, like a liquid state over a wide temperature range, an extremely low vapour pressure at RT, chemical inertness and a high heat capacity, make them an interesting material class for a wide range of applications.[1–3] They may be used in catalytic processes, in dye sensitized solar cells, or as electrolytes in electrochemical applications, to mention a few.[4,5] For example the deposition of metal nanoparticles is observed at the interface between IL and low temperature plasma discharges by electrochemical reduction of a dissolved metal salt.[6] Furthermore, the possibility of forming metal nanoparticles induced by electron beam irradiation was found recently[7,8] and it was demonstrated that a focused Ga^+ ion beam can be used for reversibly writing structures and images in frozen ILs.[9] In plasma processing as well as in material characterisation, the ionic liquids are exposed to high energy photons and electrons that can have an impact on the chemical reactions taking place or in worst case can be the cause of degradation effects in the material. Especially in some analytical methods such as photoelectron spectroscopy,[10–14] infrared spectroscopy,[15] Raman spectroscopy[16] or Auger electron spectroscopy, the ILs are exposed to different kinds of radiation by photons or electrons. A commonly used analytical method for the surface characterisation of different ionic liquids is XPS where monochromated or non-monochromated X-ray radiation is used for excitation.[17–21] Furthermore, in systems with conventional non-monochromated X-ray sources the sample surface is exposed to an additional impact of electrons that can pass through or are produced in an Al window. In contrast a monochromated source typically provides only X-ray photons since the electrons are filtered out by the geometric design of the monochromators that are used for removal of satellite lines as well as for focussing the photon beam. In XPS analyses of different imidazolium based room temperature ionic liquids, which were irradiated with monochromated AlKα radiation for a short period, no evidence of beam damage to the sample was observed.[17,22] Minimal changes in peak shape and

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stoichiometry were observed in the case of 1-ethyl-3-methyl-imidazolium ethylsulfate (ECOENG™ 212) after extended exposure time.[22]

In most experimental studies the analysis of the XPS spectra reveals a composition close to stoichiometry, which points to a relatively high stability with respect to irradiation at least for typical periods of time applied in these experiments.[13,20,22]

However, in a temperature dependent XPS study of D_2O adsorption on the surface of [OMIm]BF_4 Lovelock *et al.* described a new component in the N1s region with a binding energy 2.6 eV below the initial N1s component.[21] This component is attributed to products of beam damage and the chemical shift corresponds to nitrogen in an uncharged state. Kolbeck *et al.* observed spectral changes in their XPS measurements for many [OMIm]-based ILs after extended exposure to X-rays.[13] Most changes appeared in the N1s region at binding energies lower than that of the imidazolium nitrogen. They also suggested the presence of uncharged decomposition products.

In a recently published review Lovelock *et al.* described the effect of beam damage on the chemical state analysis and mentioned possible diffusion away from the analysed volume and segregation of degradation products as well as desorption of volatile decomposition products into the vacuum.[14]

The influence of gamma irradiation on different imidazolium-based or $[Tf_2N]^-$-based ILs is described in a few studies. The radiolysis of the imidazolium cation is mainly caused by the loss of the alkyl chains or the dehydrogenation of the carbon atom of the N–C–N bond.[23,24] During the degradation of the anion mainly F, CF_3 and CF_3SO_2 radicals are produced.[23–25]

The purpose of this work is to investigate the influence of the commonly used monochromated and non-monochromated AlKα radiation on [EMIm]Tf_2N. Therefore the IL is irradiated for five days in the case of monochromated X-rays and for over 12 hours in the case of non-monochromated AlKα. The observed changes in the spectral features are discussed in detail. An additional analysis of the residual gas components during irradiation is performed by quadrupole mass spectroscopy (QMS).

Experimental

The present experimental investigation was performed in a UHV chamber (base pressure $< 2 \times 10^{-10}$ mbar) using monochromated AlKα radiation ($h\nu = 1486.7$ eV) produced by a PHI 10-610 X-ray source (14 kV, 300 W) in combination with an Omicron XM1000 monochromator and non-monochromated AlKα radiation ($h\nu = 1486.6$ eV) generated by a conventional DAR 400 dual anode X-ray source (13 kV, 170 W), respectively, for irradiation of the samples. The distance between the aluminium window of the non-monochromated X-ray source and the sample surface was approximately 1–2 cm. The penetration depth of the used X-ray photons into the IL is in the order of several micrometres, whereas the escape depth of the emitted photoelectrons is only a few nanometres.[14] The spectra were recorded with a hemispherical electron analyser (Type EA125, Omicron) equipped with 7 channeltrons. The emitted electrons were analysed at an emission angle of $\Theta = 53°$ with respect to the surface normal. The chosen pass energy was 50 eV in the case of the survey spectra and 15 eV for the high resolution core level spectra. The operation conditions lead to a total energy resolution below 0.6 eV (FWHM of $Ag3d_{5/2}$ at a pass energy of 15 eV) for monochromated AlKα radiation and below 1.2 eV for the non-monochromated AlKα radiation, respectively. These values were determined by measurements on clean polycrystalline silver.

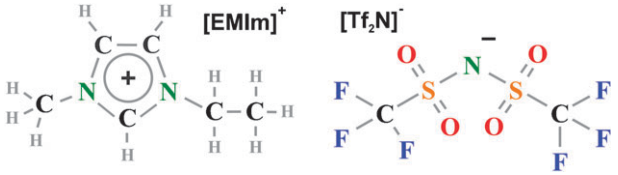

Fig. 1 Chemical structure of the cation and anion of the investigated ionic liquid [EMIm]Tf_2N.

Mass spectra were measured with a quadrupole mass spectrometer (Balzers Prisma QME 200). The complete accessible mass range of m/z from 1 to 200 amu was investigated.

The used ionic liquid [EMIm]Tf_2N was purchased from Ionic Liquids Technology (purity 99%). It has a chemical structure as depicted in Fig. 1. The sample support consists of a 250 nm thick polycrystalline Au film deposited onto Si(100), using a Ti adhesion layer in between. The samples were prepared by depositing one droplet of ultrapure RT-IL onto the Au substrate. By tilting the wafer, a uniform wetting of the surface was achieved. After outgassing in a load lock system the sample was introduced into the UHV chamber. Characterisation with monochromated XPS (AlKα) proves that this preparation technique results in stoichiometric RT-IL films. The initially measured XPS spectra are in good agreement with previous studies.[10] From the absence of any substrate (Au) related spectral feature in the XPS spectra, we conclude that the film completely covers the substrate and we estimate a film thickness of more than 10 nm for all discussed samples.[10,26] However, it is important to note that the film thickness most likely exceeds this lower limit by some orders of magnitude. If one assumes that a typical droplet with a volume of about 0.01 ml exclusively wets the entire sample surface ($\sim$1 cm^2), the resulting film thickness is in the range of $\sim$100 μm.

Results

Mass spectroscopy

A first evidence for the possible irradiation induced changes in the IL is the observed pressure increase in the UHV system during the measurements. Directly after ramping up the power of the monochromated X-ray source, a slight increase in the base pressure of the UHV chamber to 5×10^{-10} mbar is observed, which remained stable as long as the IL sample was exposed. Note that such an increase is not observed without the IL sample. A similar, but more severe effect is observed when the non-monochromated X-ray source is switched on ($p \approx 5 \times 10^{-9} - 1 \times 10^{-8}$ mbar). In contrast to irradiation with the monochromated X-ray source a minor sample heating is observed during irradiation with the non-monochromated

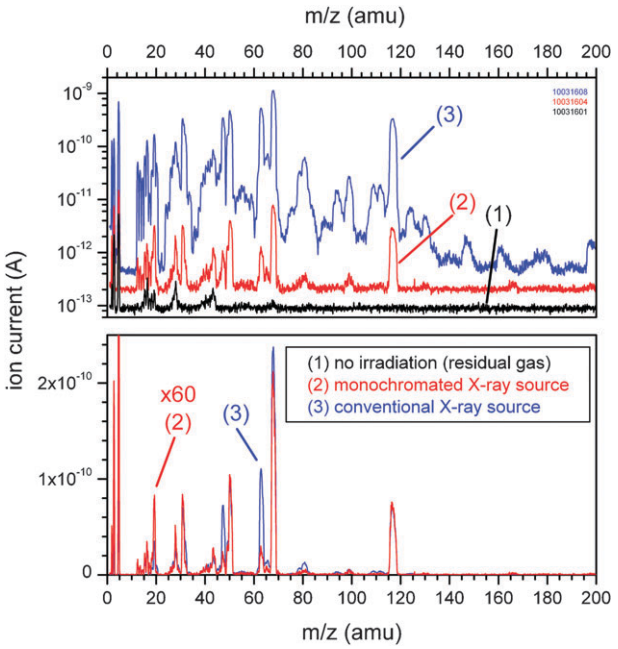

Fig. 2 QMS measurements of the gas composition in the vacuum chamber with introduced IL sample (background gas composition – (1)) and upon irradiation with a monochromated AlKα source (2) or a conventional non-monochromated X-ray source (3). The upper diagram shows the ion current in logarithmic scale. Note that an offset between the single graphs has been added for better visibility. The diagram at the bottom compares the spectra during X-ray exposure. Note that the signal of the spectrum (2) in the lower figure has been amplified by a factor of 60 in order to directly compare the relative intensities of the different features.

X-ray source (the temperature increase measured at a thermocouple which is in mechanical contact with the sample holder was about 2 K).

For a more detailed analysis of the desorbing species a residual gas analysis with and without irradiation was performed using a quadrupole mass spectrometer (see Fig. 2).

Prior to the experiments care has been taken to outgas the filaments of the X-ray sources and the mass spectrometer in advance of the degradation experiments. Consequently, desorption from hot filaments can be neglected and the detected species are due to desorption from the IL film. As visible, during X-ray exposure new components appear in the residual gas of the UHV chamber. The strongest signals are found at a mass to charge ratio (m/z) around 19, 28, 31–32, 50–51, 63–64, 68–69 and 116–118 amu. However, in both cases many other components are found in the QMS spectra as well.

As one might expect from the higher pressure rise, these peaks are more pronounced for the radiation caused by the non-monochromated X-ray source (note that the spectrum (2) in the lower part of Fig. 2 is enhanced by a factor of 60 for comparison). This assumption is indeed confirmed, but the desorbed species are almost identical for both cases. Only noticeable differences in the intensity ratio are found for the features at 47–48, 63–64 and 78–81 amu. Switching off the X-ray sources resulted in an abrupt reduction of the signal intensity in the quadrupole mass spectrogram.

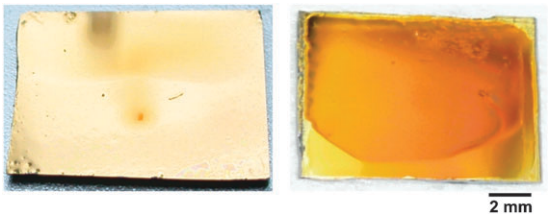

Fig. 3 Photographs of [EMIm]Tf_2N films on the Au/Ti/Si template after 5 days irradiation with monochromated (and focussed) AlKα radiation (left picture) and after 12 hours exposure using a conventional X-ray source (right picture).

However, for comparison of the quantities of the ion current one has to consider that the photon fluxes at the sample surface as well as exposed area are different comparing the results for the used monochromated and non-monochromated X-ray sources. This is apparently represented by the visible appearance of the IL after long exposure. Fig. 3 compares photographs of IL films on Au after X-ray irradiation. An apparent colour change is found in the illuminated sample area. As can be seen the altered spot has a diameter of ~3/4 mm. In the following discussion we assume a Gaussian beam profile of the monochromated X-ray beam with a FWHM of 3/4 mm, which is in line with the specifications of the used source. For the non-monochromated X-ray beam, the entire IL-film area is altered.

A similar colour change together with a strong pressure increase ($p \approx 2 \times 10^{-8}$ mbar) is observed during the bombardment of the IL with high energy electrons (3 kV).

XPS results

(i) Initial state of the IL film. For the freshly prepared surfaces besides the elements that are present in the chemical structure of [EMIm]Tf_2N (carbon, nitrogen, sulfur, fluorine and oxygen) no impurities are found in the measurements. The observed peak separation due to the different chemical bonds as well as the peak area ratio reflects the chemical structure and composition of the IL well.[10] Especially the formerly observed additional amount of carbon impurities in our experiments is absent in these measurements due to improved sample preparation.

(ii) Radiation-induced changes. Variation of the chemical composition due to X-ray exposure can be directly measured by continuous XPS measurements. For this purpose we have performed long time experiments acquiring spectra upon perpetual irradiation. The changes in the XPS core level spectra reveal that the near surface chemical composition is altered by excessive irradiation.

The results of these series are exemplarily represented by the C1s, N1s and S2p spectra shown in Fig. 4 and 5 after irradiating [EMIm]Tf_2N for a period of 5 days by monochromated AlKα and for 12 hours by non-monochromated AlKα radiation, respectively. It has to be mentioned that, for better comparison, the measurements in Fig. 5 (except that of the top spectra) were also performed using the monochromated AlKα source in order to take advantage of the better energy resolution to identify the emerging chemical changes. For this purpose, a periodic series was performed

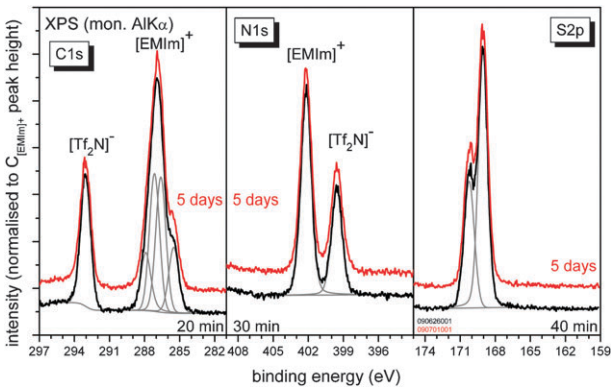

Fig. 4 C1s, N1s and S2p spectra of [EMIm]Tf_2N during the first scan (acquisition time ≈ 30 min) including peak fit of the different components (bottom) and after 5 days continuous irradiation with the monochromated X-ray source (top). The spectra are plotted with a vertical offset.

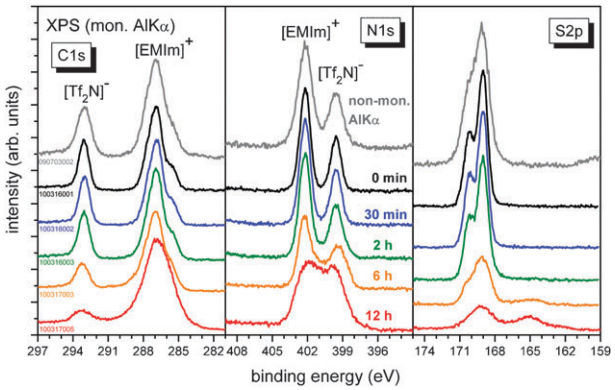

Fig. 5 C1s, N1s and S2p spectra of [EMIm]Tf_2N after irradiation with the conventional dual anode X-ray source after 0, $\frac{1}{2}$, 2, 6 and 12 hours acquired with the monochromated X-ray source. For comparison the top curves show the spectra measured with the non-monochromated source.

by irradiating the sample with the conventional X-ray source for a certain time before switching it off for XPS analysis with the monochromated source and finally proceeding with the irradiation for the next cycle. As will be shown below, the interruption of the exposure together with the irradiation of the sample with the monochromated source for XPS analysis has a negligible influence on the chemical properties during this measurement interval.

As visible in Fig. 4 and 5 the changes appear on different time scales and are obviously less pronounced for the monochromated AlKα source. Again as in the case of the analysis of QMS quantities, the interpretation of the observed results needs to consider the different applied fluxes for the X-ray sources (see discussion). In more detail, the following changes are observed.

(a) Monochromated source. For the exposure to X-rays from the monochromated source only minor changes in the peak shape are observed even after 5 days of continuous X-ray impact. Apart from these minor effects, there is almost no change in the observed full width at half maximum of the peaks related to the different carbon bonds (CF_3, N–C–N, C–C–N, C–C).

(b) Non-monochromated source. In contrast, the non-monochromated source induces more pronounced changes at a shorter time scale. After irradiation, strong changes in the relative peak intensities and the stoichiometry of the sample are observed. The amount of sulfur, fluorine and oxygen is reduced, whereas the total signals from the nitrogen and carbon states gain in intensity.

By fitting the peak area of the F1s, O1s, N1s, C1s and S2s states and assuming a homogeneous elemental distribution, the chemical changes in the stoichiometry of the IL film can be quantified. Table 1 summarises the results of this estimation and provides information on the quantitative changes. Most remarkable is that the amounts of fluorine, oxygen and sulfur are reduced to approximately half of their initial values while the amounts of nitrogen and carbon increased by 53% and 43%, respectively.

Moreover the spectral shape of the single components is strongly modified. The most remarkable effect could be observed in the S2p and N1s spectra accompanied by a change in the ratio of the single components in the C1s signal (see Fig. 5). In the O1s and F1s spectra (not shown) only a slight asymmetry at the low binding energy side is observed while the FWHM of all observed peaks increased slightly during the

Table 1 Quantification of the changes in surface elemental composition of [EMIm]Tf_2N upon X-ray exposure for the monochromated and non-monochromated excitation source. The nominal ratio (deduced from chemical structure) and the measured values are given in at.% while the variation is given in % referring to the numbers after short exposure. For nitrogen and carbon the contributions of the cation (cat) and the anion (an) are listed in brackets

	F	O	N (N^{cat} + N^{an})	C (C^{cat} + C^{an})	S
Nominal	26.1	17.4	13.0 (8.7 + 4.3)	34.8 (26.1 + 8.7)	8.7
Monochromated X-rays					
Short exposure	23.5	15.9	13.0 (8.3 + 4.7)	38.5 (28.9 + 9.6)	9.1
5 days exposure	23.5	15.2	13.2 (8.4 + 4.8)	38.8 (29.0 + 9.7)	9.3
Variation (5 d)	±0%	−4%	+2%	+1%	+2%
Non-monochromated X-rays					
Short exposure	23.8	15.6	13.1 (8.9 + 4.3)	38.6 (28.4 + 10.2)	8.9
30 min exposure	23.0	15.0	14.5 (9.5 + 5.0)	38.3 (29.0 + 9.3)	9.2
2 h exposure	22.9	13.9	14.9 (9.3 + 5.5)	40.0 (30.6 + 9.4)	8.3
6 h exposure	20.5	10.4	16.8 (9.3 + 7.5)	46.7 (39.3 + 7.4)	5.5
12 h exposure	13.5	7.3	20.0	55.2 (50.9 + 4.2)	4.1
Variation (12 h)	−43%	−53%	+53%	+43%	−54%

irradiation period. From the changes in the C1s spectrum one can deduce a reduction of the peak intensity related to the CF_3 groups at 293.1 eV giving a first hint that especially the $[Tf_2N]^-$ anion undergoes strong radiation induced changes.

Furthermore a shoulder is formed around 288.7 eV at the tail of the C1s emission related to the $[EMIm]^+$ cation. In the case of the N1s feature an increased intensity between the two chemical components of the neat ionic liquid between 402.2 eV and 399.6 eV is found. The most drastic effect is observed for the sulfur atoms. Besides the strong decrease of the initial emission of the S2p state ($S2p_{3/2}$ at 169.0 eV) a new feature is formed at $\sim$165 eV exhibiting a relatively large chemical shift.

One further result should be mentioned. Due to the strong modification of $[EMIm]Tf_2N$ upon irradiation, after 12 hours of exposure to the non-monochromated X-rays the ionic liquid lost its conductive character. The reduction of the IL conductivity results in charging of the surface during the XPS measurement. All spectral features shift up to $\sim$15 eV towards lower kinetic energy. In order to minimise this shift as well as the broadening of the core level spectra due to surface charging, a conventional charge neutraliser, providing low energy electrons, was employed for the measurements after 12 hours (lowermost spectra in Fig. 5). A slight broadening is inevitable, but this effect has no influence on a detailed analysis of the degradation processes.

Discussion

The calculated chemical composition based on the quantification of the peak areas after short X-ray exposure leads to a F : O : N : C : S ratio which is close to the expected ratio for the neat IL sample. The results of the quantitative analysis are summarised in Table 1. For the calculation of the stoichiometry a transmission function $T = 1/E_{kin}$ is assumed. The deviation of the nominal values of $[EMIm]Tf_2N$ ($C_8H_{11}N_3S_2O_4F_6$) to the measured values after short exposure of the sample is most likely due to this improper analyser transmission function. Using the relative peak areas of the C1s and N1s for the calculation of the anion/cation ratio led to good agreement with the nominal values.

Therefore we have obviously prepared a clean IL surface and moreover, the relatively short X-ray irradiation period with the monochromated X-ray source did not alter the chemical surface composition.

Before a more detailed discussion of the observed changes in the QMS and XPS spectra, some considerations regarding the intensity and flux provided by the used X-ray sources are necessary.

(i) Estimation of the relative fluxes and intensities provided by the used X-ray sources

As already pointed out, the comparison of the results (XPS and QMS) for the different sources that have been applied has to consider the respective photon flux and area of illumination. For a quantitative estimation we use the intensity of the emitted F1s electrons under the same analyser conditions in the XPS spectra. For the monochromated X-ray source the number of detected electrons is 6.5 times lower compared to the excitation using the non-monochromated source (N_{non}/N_{mon} = 6.5). For the quantification we assume a homogeneous illumination of the entire sample (sample area $\approx$ 1 cm^2) for the non-monochromated source, whereas the monochromated source provides a focussed X-ray beam. The spot diameter lies in the range of 1 mm, which is in line with the observed region, where a strong colour change is observed (Fig. 3). According to the specifications of the source the profile can be described by an axially symmetric Gaussian profile with a FWHM of 0.75 mm ($G_{0.75}$). Furthermore one has to consider that the analyser collects electrons from a certain sample area. According to the analyser specifications the chosen operation conditions lead to a nearly Gaussian profile with a FWHM of 1.5 mm ($G_{1.5}$). With these numbers the effective maximum photon flux ratio and the number of photons hitting the sample that result in different QMS signals can be estimated by

$$\frac{F_{non}}{F_{mon}} = \frac{N_{non} \cdot \{G_{0.75} \otimes G_{1.5}\}}{N_{mon} \cdot G_{1.5}}$$

and

$$\frac{I_{non}^{QMS}}{I_{mon}^{QMS}} = \frac{N_{non}}{N_{mon}} \frac{100 \cdot \{G_{0.75} \otimes G_{1.5}\}}{\{G_{0.75}\} \cdot \{G_{1.5}\}}$$

with $\{f(r)\} = \int f(r) d^3r$ being the volume integral of the Gaussian profiles. The resulting ratios are F_{non}/F_{mon} = 1.3 and $I_{non}^{QMS}/I_{mon}^{QMS}$ = 37, respectively.

(ii) Mass spectroscopy

Based on this consideration it is evident that the increased pressure rise (by a factor of 60) is in the same order of magnitude as the difference in the total amount of photons impacting the IL film per second. Furthermore, the acquired mass spectra are rather similar as far as the detected masses and their relative intensities are concerned.

The peaks at the mass to charge ratio (m/z) of 19, 28, 31–32, 50–51, 63–64, 68–69 and 116–118 amu can be attributed to different fragments of the $[Tf_2N]^-$ anion, like F, CF, CF_2, SO_2, CF_3, and CF_3SO. Günster *et al.* also observed similar fragments which originate from the $[Tf_2N]^-$ anion like F (19 amu), CF (31 amu) or CF_3 (69 amu) in positive and negative SIMS spectra of $[EMIm]Tf_2N$.[27] Other time of flight mass spectrometry studies also identified the m/z ratio of 69 with CF_3^+ ions generated due to decomposition of the $[Tf_2N]^-$ anion.[28,29] From degradation studies of fluorocarbon films it is well known that the CF_3 groups do not sustain X-rays and decompose upon comparable photon fluxes.[30] However it has to be mentioned that the peak at m/z = 69 amu can also be assigned to $C_3H_5N_2$ related to fragments from $[EMIm]^+$ ions and the signal at m/z = 28 amu might be associated to C_2H_4.

The relatively stronger desorption of species related to the QMS features at 47–48, 63–64 and 78–81 amu could be related to additional decomposition processes that might *e.g.* involve the scattered electrons from the non-monochromated X-ray source that hit the surface as well. Otherwise the increasing sample temperature due to irradiation with the non-monochromated X-ray source could lead to increased diffusion of these decomposition products. However, only minor

temperature changes close to the sample have been observed. Nevertheless, based on the obtained results from the QMS spectra, it can be concluded that the desorbing species are rather independent of the used source and are indeed roughly proportional to the X-ray photon flux. Furthermore, the detected colour change after excessive irradiation is a strong indication that the IL sample is altered during exposure. Finally the proof that the detected peaks in the mass spectra are strongly correlated with the X-ray irradiation can be deduced from the fact that the residual gas composition recovered immediately after switching off the X-ray sources.

(iii) X-Ray photoelectron spectroscopy

In order to acquire information on the chemical changes related to the remaining IL film it is worth to analyse the XPS measurements. First conclusions on the underlying degradation processes can be drawn from the analysis of the changes in elemental composition of the surface, which is summarised in Table 1. The stoichiometry after a short irradiation time is in good agreement with respect to each other and the nominal elemental ratio of the neat IL. However, after excessive irradiation changes in the stoichiometry of the sample are observed.

Moreover, the presented experiments show strong differences in the resulting IL surface composition for the two X-ray sources used. First of all the X-ray induced changes are almost two orders of magnitude slower for the monochromated source. However, these changes are expected to be rather similar, since the maximum photon flux across the analysed area is comparable. Even when comparing the data for 5 days irradiation by the monochromated source with those for 2 hours irradiation utilising the non-monochromated source (reflecting the factor of 60 detected in the QMS data) one already realises changes for the non-monochromated source. One difference between the two X-ray sources is that – in contrast to the monochromated source – the non-monochromated source obviously leads to new components in the high resolution scans of the single elements. Note that one would have to assume a high diffusivity of the formed species to explain the different time dependence by a factor of 60. However, from the stability of the observed colour change we tend to exclude a strong diffusion of the formed species, although we are aware of the possibility that the decomposition could mainly take place at the Au–IL interface, induced *e.g.* by secondary electrons generated in the substrate by the X-rays that penetrate the IL film. In this case the colour change should be proportional to the X-ray exposure, which means that a stronger colour change would be expected for the monochromated source (see Fig. 3a). Furthermore, first experiments utilising a high intensity electron beam (energy 10 eV) as provided by a flood gun causes only minor colour changes even after excessive irradiation, which seems to indicate that low energy electrons might not be crucial. Moreover, we observe comparatively strong charging effects after excessive irradiation and the fluidic properties (viscosity) are altered as judged from visual inspection of the samples after the experiments. These observations indicate a lower diffusivity of the reaction products compared to the self-diffusion of the ions in the neat IL. In addition, we observe a similar colour change if the sample is irradiated by fast electrons, although in this case the electrons do not reach the IL–substrate interface. Therefore, we tend to exclude that the colour change is at least solely at the interface.

One possible reason for the observed differences in the temporal behaviour of the XPS spectra for the two X-ray sources used is that electrons which are generated in the non-monochromated X-ray source are responsible for additional beam damage effects, which is in line with the observation that fast electrons lead to similar changes. Due to the small increase of the temperature at the sample holder we tend to exclude thermal effects such as a thermally increased diffusion in the case of the non-monochromated source. Due to the observed differences we will discuss the changes in more detail separately.

(a) Monochromated source. In the case of the monochromated source, the oxygen signal looses slightly in intensity while the intensity of the sulfur, nitrogen, carbon and fluorine signals is almost constant. There is no indication for any new chemical component in the spectra. The main effect is related to a reduction of the relative amount of CF_3 groups that might be most fragile and accompanied by the excitation and desorption of oxygen atoms from the $[Tf_2N]^-$ ion. Reordering effects of the remaining functional groups that cannot be taken into account in the quantification could cause the minor discrepancy between the calculated composition and the chemical changes.

(b) Non-monochromated source. In the case of 12 hours exposure to X-rays from the non-monochromated source, the amount of fluorine, oxygen, and sulfur decreased by 10.3, 8.3 and 4.8 at.%, respectively, which corresponds to a reduction to about one half of the initial values. On the other side, the amount of carbon and nitrogen increased by 16.6 and 6.9 at.%.

Concerning the microscopic variation of the chemical structure under the influence of the non-monochromated X-ray source important statements can be deduced from the analysis of the changes in the different contributions to the C1s, N1s, O1s, F1s and S2p peak shape. As already mentioned, the F1s and O1s spectra reveal the formation of a negligible shoulder at the low binding energy, but no direct indication for the formation of different chemical bonds is found while the total intensity of oxygen and fluorine is continuously decreasing.

The cation to anion ratio which can be directly quantified by comparison of the different contributions in the N1s and C1s measurements increased during ongoing irradiation. At the beginning of the irradiation the signal ratio of the carbon states from $[EMIm]^+$ and $[Tf_2N]^-$ ions was 6 : 2, calculated from the peak area ratio of the peaks related to $[EMIm]^+$ and $[Tf_2N]^-$ in the C1s spectrum using 5 components related to the different chemical states in $[EMIm]Tf_2N$ (see Fig. 4 and Ref. 10) which is in agreement with the nominal ratio. After 12 hours of irradiation with non-monochromated AlKα radiation the ratio changed to 24 : 2. Nevertheless, the spectral shape of the C1s region is also changed, especially the

broadening of the high energy tail of the signal related to the $[EMIm]^+$ states in the C1s spectrum has to be mentioned that could be related to reconfiguration of the neighbouring ions or molecules.

In the case of the N1s peak, the ratio of nitrogen atoms in the cation and anion was initially also as expected ~2 : 1. However the increased intensity between the two chemical components of the neat ionic liquid at 402.2 eV and 399.6 eV makes a clear separation after longer exposure difficult. The origin of this new structure at ~400.5 eV could be related to the generation of neutral imidazole species. Nolting *et al.* investigated aqueous imidazole at different pH-values using photoelectron spectroscopy. They observed a single peak in the N1s region for cationic imidazole (both nitrogen atoms are chemically equivalent) and two components, which differ 2.7 eV in binding energy, for neutral imidazole where only one nitrogen atom is saturated by a hydrogen atom.[31] They determined the chemical shift induced by the single hydrogen bond to be ~1.7 eV and the chemical shift induced by delocalised charge to be ~1.0 eV. A similar structure, which is addressed to beam damage, was observed by Lovelock *et al.* during water adsorption studies on $[OMIm]BF_4$.[21]

Furthermore Shkrob *et al.* suggested that aromatic cations, especially imidazolium based cations, serve as electron-trapping centres during radiolysis resulting in the formation of neutral radicals and radical ions.[32,33]

In addition the formation of the new component at 165 eV in the S2p signal gives the final experimental hint for a tentative description of the degradation processes. Obviously the $[Tf_2N]^-$ ions are heavily altered due to the impacting X-ray photons and electrons. Fragments of the bis(trifluoromethyl-sulfonyl)imide ions desorb from the IL surface and new chemical species are remaining in the film. While especially the CF_3 groups are split off as well as the oxygen atoms are removed, some of the sulfur and nitrogen atoms remain at the surface and reconfigure together with the 1-ethyl-3-methyl-imidazolium ions to new complex structures. Although there is no indication for a direct decomposition of the $[EMIm]^+$ ion upon exposure, the changing environment as well as the remaining charged molecules lead to an electron transfer especially towards the nitrogen atoms in the imidazolium ring. This transfer of effective charge results in the shift of the binding energy and hence explains the rising feature at ~400.5 eV in the N1s measurement. The different carbon bonds in the imidazolium ring are also affected and hence the relative peak areas are changed and the shoulder with a higher binding energy than the initial N–C–N bond at 402.2 eV is formed. Part of the sulfur atoms are actually changing their chemical state.

In pulse radiolysis studies indications for the formation of neutral radicals by electrons which attack the ring of aromatic cations such as imidazolium and pyridinium are found.[34] These experiments give hints that indeed the electrons which are generated in the non-monochromated X-ray source also could be responsible for the beam damage effects.

Overall one has to expect that both sources of energy that impact the surface (X-rays and electrons) are responsible for the effects that lead to degradation of the surface of the ionic liquid film, possibly having different reactions constants.

Although a reliable identification of the formed species is not possible yet, this aspect implies that intensive irradiation by non-monochromated X-rays might alter the IL properties much stronger compared to monochromated X-rays. This finding is *e.g.* important for thickness-dependent experiments, where IL films are successively evaporated onto a substrate, as recently performed by Cremer *et al.*[35]

(c) Comparison to other ILs. Finally, one should note that the impact of the irradiation on the IL composition seems to be dependent on the particular choice of IL. Therefore, one has to consider these effects carefully, although the changes are typically rather small within the typical time frame for a single XPS analysis. Nevertheless, in the case of the [EMIm]FAP, which is the most sensitive IL we have investigated so far, we observed changes in the range of 10% already after 3 h irradiation, even if the monochromated source was used. Moreover, at present it remains unclear whether possible trace amounts of impurities might alter the photon-induced degradation.

Conclusions

In the present work, we have studied the influence of AlKα X-rays on the ionic liquid $[EMIm]Tf_2N$. Monochromated X-ray exposure over a long period leads to almost negligible degradation effects. In contrast non-monochromated AlKα sources, with around 1.3 times higher maximum photon flux and larger exposure area, showed strong degradation effects after only a few hours. This leads to the conclusion that the electrons strongly increase the degradation effect for conventional X-ray laboratory sources often employed in XPS measurements. Sample treatment with high energy electrons from an electron gun confirms this behaviour of strong degradation of $[EMIm]Tf_2N$. A pressure rise in the UHV chamber during X-ray irradiation of the sample is a good indicator for sample degradation and a detailed analysis of the volatile degradation products can be performed by QMS. In general the $[Tf_2N]^-$ anion seems to be more affected by beam damage than the imidazolium cation. For imidazolium based ionic liquids it can be stated that the time frame for XPS measurements employing monochromated X-ray sources is rather large compared to commonly required times for spectra acquisition. However, minor changes in the chemical composition and structure occur in this case as well.

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